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Introduction

The advanced regeneratively cooled rocket thrust chamber may require new materials to achieve long life and improved performance. The materials need high thermal conductivities to maximize heat exchange and minimize temperature gradients. The new materials must also be more creep resistant and have higher temperature capability than previously used alloys. Current materials such as NARloy-Z (Cu-3 wt.% Ag-0.5 wt.% Zr) while highly conductive do not have sufficient high temperature strength and creep resistance to meet the needs of advanced rocket motors. NASA Lewis Research Center has undertaken a program to develop new materials to meet the anticipated needs. One promising alloy identified is a copper - 8 at.% chromium - 4 at.% niobium (Cu-8 Cr-4 Nb) alloy (1,2). The alloy is strengthened by Cr_2Nb intermetallic precipitates dispersed throughout the Cu matrix.

A major concern with using the alloy in a regeneratively cooled rocket nozzle is the presence of large amounts of liquid and high pressure gaseous hydrogen. It is well known that niobium can form a hydride (3). If this occurs in the Cu-8 Cr-4 Nb alloy it could lead to hydrogen embrittlement. A thermodynamic analysis of the alloy was undertaken to determine the potential for niobium hydride formation. Samples of the alloy were also exposed in high pressure gaseous hydrogen and tensile tested to determine if any hydrogen embrittlement occurred.

Thermodynamic Analysis

Reaction of Nb with H_2 results in the formation of niobium hydride (NbH). The Nb-H phase diagram (3) shows a β phase with a homogeneity range of 41 to 51 at. % H. The β phase is not stable above 418 K. Although pure Nb reacts with H_2 to form a niobium hydride, reaction of Nb-containing compounds such as Cr_2Nb with H_2 will be a function of the activity of Nb in the compound. Thermodynamic calculations were performed to examine if niobium hydride can form by the reaction of Cr_2Nb with H_2 .

The compound Cr_2Nb is nonstoichiometric (4) and can exist over a narrow composition range. For Cr_2Nb in equilibrium with the Nb-rich solid solution, the activity of Nb is close to unity, and its reaction with H_2 will essentially be the same as that of pure Nb. The activity of Nb in Cr-rich Cr_2Nb is less than unity and can be calculated from the equilibria for the reaction

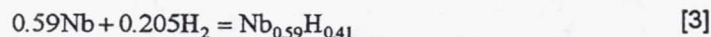


for which the equilibrium constant (K_1) is

$$K_1 = \frac{1}{(a_{\text{Cr}})^2 (a_{\text{Nb}})} \quad [2]$$

where a_{Cr} and a_{Nb} are activities of Cr and Nb in Cr_2Nb , respectively. The underlines in Reaction [1] denote reduced activities for the elements. The Nb content in Cr-rich solid solution in equilibrium with Cr_2Nb is < 1 at. % for temperatures lower than 1273 K. Thus, a_{Cr} in Cr-rich Cr_2Nb can be assumed to be unity. Using the Gibbs free energy of formation data from the compilation by Barin (5), the activity of Nb in Cr-rich Cr_2Nb was calculated to be 2.15×10^{-4} at 298 K, 1.16×10^{-3} at 373 K, and 0.011 at 573 K.

Consider the reaction of Cr-rich Cr_2Nb with H_2 to form a niobium hydride of composition $Nb_{0.59}H_{0.41}$ (H/Nb ~0.7), which can be written as:



Using the thermodynamic data of Albrecht et al. (6) for $Nb_{0.59}H_{0.41}$, the equilibrium partial pressure of H_2 (p_{H_2}) for the formation of $Nb_{0.59}H_{0.41}$ was calculated from the equilibria for Reaction [3]:

$$K_3 = \frac{1}{(a_{Nb})^{0.59} (p_{H_2})^{0.205}} \quad [4]$$

Table I gives the equilibrium partial pressure for Reaction [3] corresponding to the reaction of Cr-rich Cr_2Nb and pure Nb (or Nb-rich Cr_2Nb).

The H_2 pressures shown in Table I are the minimum H_2 pressure required for the formation of $Nb_{0.59}H_{0.41}$ (6). Although very small hydrogen pressures are required for the reaction of pure Nb to form a niobium hydride, substantially greater (about nine orders of magnitude higher) H_2 pressures are required for the reaction of Cr-rich Cr_2Nb to form a niobium hydride. Table I shows the H_2 pressures required for the formation of $Nb_{0.59}H_{0.41}$, which represents the Nb-rich boundary of the NbH phase, from Cr-rich Cr_2Nb . The corresponding H_2 pressures will even be higher for NbH with H contents greater than 41 at. %. For example, the equilibrium H_2 pressure for the reaction of Cr-rich Cr_2Nb to form niobium hydride with a H/Nb ratio of 0.85 is 1.024×10^5 MPa at 373 K, as compared to 462.2 MPa for a H/Nb ratio of 0.7.

The β NbH phase is not stable above 418 K (3). However, a Nb-H solid solution forms at high temperatures. The feasibility of forming a Nb-H solid solution can be examined from thermodynamic considerations by treating the solid solution of any given composition as a compound. For example, consider the formation of a Nb-H solid solution at 573 K with a H/Nb ratio of 0.1. The solid solution of this composition can be treated as a compound of composition $Nb_{0.91}H_{0.09}$, and the reaction of Cr_2Nb to form this compound can be written as:



Based on the thermodynamic data of Albrecht et al. (6), the equilibrium partial pressure of H_2 for Reaction [5] corresponding to the reaction of Cr-rich Cr_2Nb ($a_{Nb} = 0.011$) to form $Nb_{0.91}H_{0.09}$ is 5.36×10^{35} MPa; the corresponding H_2 partial pressure for the reaction of pure Nb is 3.2×10^{-4} MPa (6).

Experimental Procedure

A bar of Cu-8 Cr-4 Nb alloy was produced by extruding commercially atomized powder as described elsewhere (1). The composition of the alloy is presented in Table II. Four tensile test samples were sent to NASA Marshall Space Flight Center for testing in high pressure gaseous hydrogen. The first two samples used a subsize notched sample design machined as specified by ASTM Standard 292 (7) to determine if the material would become notch sensitive after exposure to hydrogen. The specimen design gave a stress concentration factor (K_t) of 3.9 in the notch region. The two notched samples were tested at room temperature in a 34.5 MPa (5,000 psi) hydrogen gas environment. The two smooth samples were a conventional subsize tensile test specimen design machined as specified by ASTM Standard E 8 (8). The smooth samples were cycled from ambient temperature to 978 K (1300°F) to

ambient in a 34.5 MPa gaseous hydrogen environment three times. Following exposure, the samples were tested at room temperature in a 34.5 MPa gaseous hydrogen environment.

Following tensile testing, the fracture surfaces were examined optically and with an SEM to determine if any change in fracture mechanism could be observed. The fracture surface was also examined for any evidence of hydride formation

Results and Discussion

Thermodynamic Analysis

Thermodynamic data show that the reaction of Nb-rich Cr_2Nb (for which the Nb activity is close to unity) is more favorable than that of Cr-rich Cr_2Nb . However, any reaction of the Nb component in Cr_2Nb will quickly move the Cr_2Nb composition toward the Cr-rich boundary. Thus, for all practical purposes, the reaction of Cr-rich Cr_2Nb with H_2 will determine the stability of Cr_2Nb in H_2 .

From Table I, the equilibrium partial pressures of H_2 for reaction of Cr-rich Cr_2Nb to form $\text{Nb}_{0.59}\text{H}_{0.41}$ are less than 35 MPa, a typical rocket motor operating pressure, at both room temperature and 323 K, but greater than 35 MPa at 373 K and higher temperatures. The H_2 pressures required for the formation of a Nb-H solid solution are considerably higher than 35 MPa for the reaction of Cr-rich Cr_2Nb . Thus, Cr-rich Cr_2Nb can react with H_2 at 35 MPa pressure to form a niobium hydride at room temperature and 323 K, but can be considered to be chemically stable in 35 MPa H_2 at temperatures greater than ~373 K. No Nb-H solid solution will form at any of these temperatures. This implies good stability of the alloy at elevated temperatures in a hydrogen environment.

Tensile Testing

The notched samples both failed in the smooth portion of the sample, indicating that the materials did not become notch sensitive following hydrogen exposure. The strength and ductility of the hydrogen exposed material are presented in Figures 1 and 2 respectively. The properties of unexposed samples from a previous study (1) are also presented. A slight increase in strength was observed in the samples exposed to the hydrogen environment, but the increase fell well within the variation of the strengths of the unexposed samples. The elongation of the three sets of samples was nearly identical. The reduction in area for the uncycled samples showed an increase over the reduction in area for unexposed samples while the cycled samples showed a decrease in the reduction in area. The values still fall within the limits of previously tested unexposed samples. No gross decrease in the measured ductility of the material was observed. This strongly indicates that the Cu-8 Cr-4 Nb alloy was not hydrogen embrittled under the test conditions.

Typical fracture surfaces for unexposed and hydrogen exposed samples are presented in Figures 3 and 4. Comparing the two fracture surfaces, there is no apparent change in the fracture mechanism. Microvoid coalescence and growth are occurring in both samples. No significant change in dimple size was observed. In Figure 4, a large precipitate of Cr_2Nb can be observed on the fracture surface. Even at magnifications up to 60,000X there was no evidence of hydride formation visible on the surface of the precipitates or anywhere else on the fracture surface. There were also no pits indicating that hydrides formed but were lost during tensile testing.

Although reaction of Cr_2Nb with 35 MPa H_2 to form a niobium hydride is thermodynamically feasible at room temperature and 323 K, the kinetics of the reaction appear to be extremely slow at such low temperatures. This is probably the reason why no reaction was observed between Cr_2Nb and H_2 at a gas pressure of 35 MPa and no degradation of mechanical properties occurred.

Conclusions

Thermodynamic analysis of the alloy indicates that the alloy could potentially form NbH at low temperatures and high pressures given sufficient time. Above 373 K the material cannot form NbH except at extreme pressures. However, room temperature tensile testing of samples exposed to high pressure hydrogen and analysis of the fracture surfaces show no hydrogen embrittlement or notch sensitivity. This indicates that the kinetics for the formation of NbH are very slow at room temperature even when the material is saturated throughout the sample with hydrogen. The alloy is therefore suitable for use in high pressure hydrogen environments and in particular rocket thrust chambers.

Acknowledgments

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References

- (1) D.L. Ellis and R.L. Dreshfield, *Proc. of the Adv. Earth-to-Orbit Conf., Vol. I*, CP 3174, NASA MSFC, Huntsville, AL, (1992), pp. 18-27
- (2) D.L. Ellis and G.M. Michal, NASA CR-185144, NASA, Washington, DC (Sept. 1989)
- (3) J.F. Smith, *Bull. Alloy Phase Dia.*, Vol. 4, No. 1 (1983), pp. 39-46
- (4) M. Venkatraman and J. P. Neumann, *Bull. Alloy Phase Dia.*, Vol. 7, (1986) pp. 462 - 466
- (5) I. Barin, *Thermochemical Data of Pure Substances, Part I*, VCH Verlagsgesellschaft mbH, D-6940 Weinheim, Federal Republic of Germany (1989)
- (6) W. M. Albrecht, M. W. Mallett, and W. D. Goode, *J. Electrochem. Soc.*, Vol. 105, (1958) pp. 219-223
- (7) *1992 Annual Book of ASTM Standards, Vol. 03.01*, ASTM, Philadelphia, PA (1992), pp. 433-441
- (8) *Ibid*, pp. 130-149

TABLE I

Equilibrium partial pressure of H₂ for the reaction $0.59 \text{ Nb} + 0.205 \text{ H}_2 = \text{Nb}_{0.59}\text{H}_{0.41}$

Temperature (K)	p _{H₂} for Cr-rich Cr ₂ Nb (MPa)	p _{H₂} for pure Nb (MPa)
298	1.98	6.74×10^{-11}
323	6.4	1.42×10^{-9}
373	462.2	1.93×10^{-6}

Table II

Chemical Composition of Cu-8 Cr-4 Nb Alloy

Element	Atomic Percent	Weight Percent
Cu	87.8	88.2
Cr	8.3	6.0
Nb	3.9	5.8
O	-	640 ppm

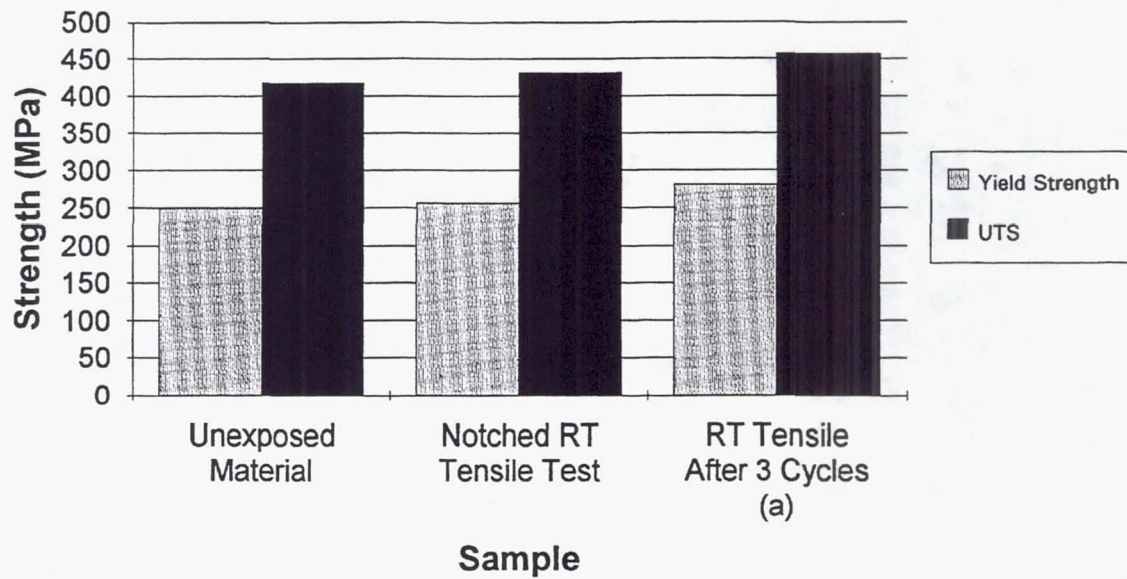


Fig. 1 - Average Room Temperature Strength of Cu-8 Cr-4 Nb Before and After Hydrogen Exposure.
(a) Smooth Samples Cycled From Room Temperature To 978 K Three Times.

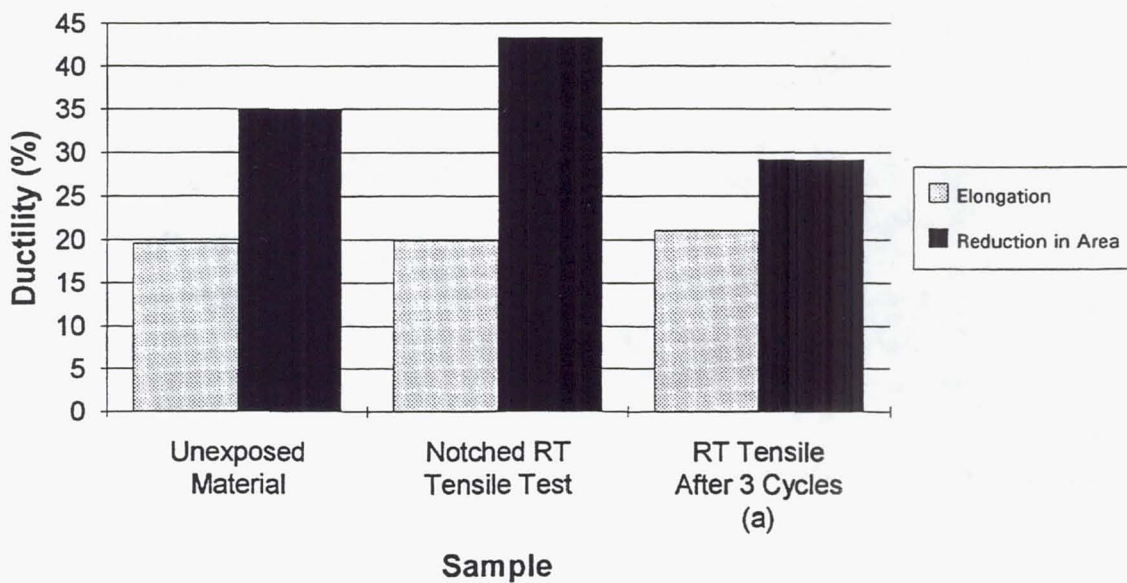


Fig. 2 - Average Room Temperature Ductility of Cu-8 Cr-4 Nb Before and After Hydrogen Exposure.
(a) Smooth Samples Cycled From Room Temperature To 978 K Three Times.

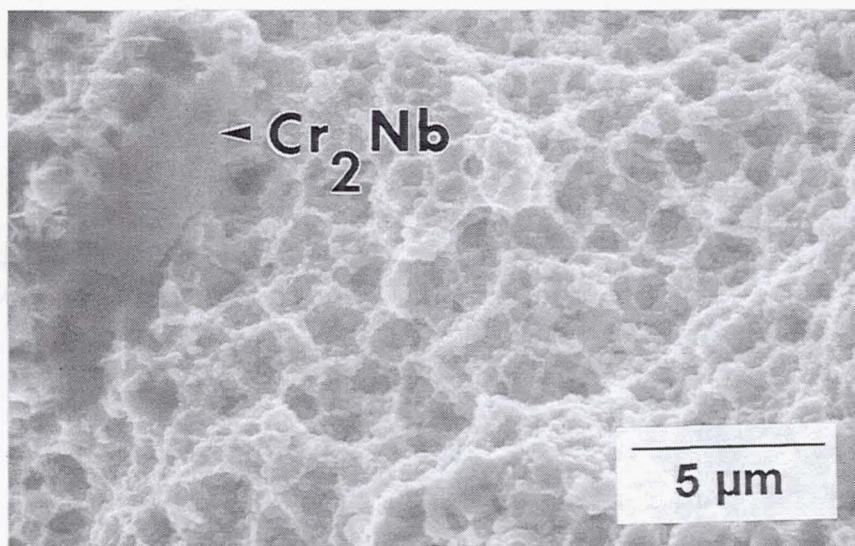


Fig. 3 - Typical Fracture Surface of Unexposed Cu-8 Cr-4 Nb Tensile Test Specimen

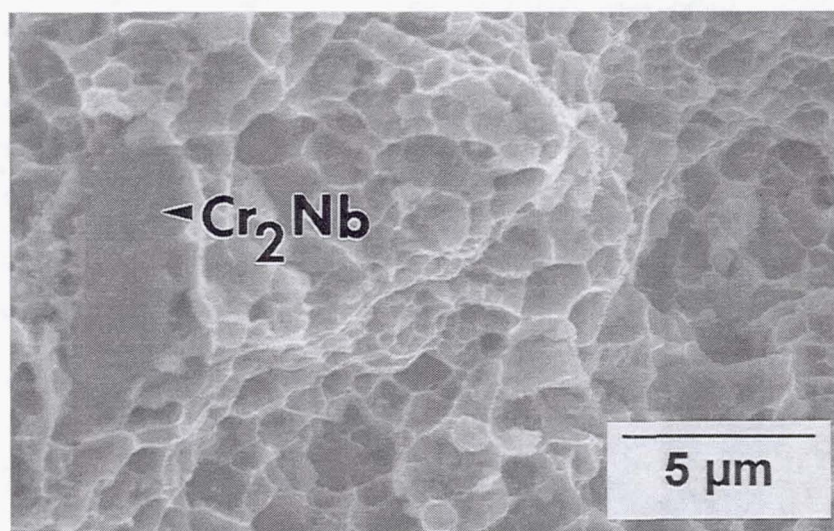


Fig. 4 - Typical Fracture Surface of Hydrogen Exposed Cu-8 Cr-4 Nb Tensile Test Specimen

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